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STUDIES OF THIOBENZOYL ISOCYANATE—I

REACTION OF THIOBENZOYL ISOCYANATE WITH HYDRAZINES*

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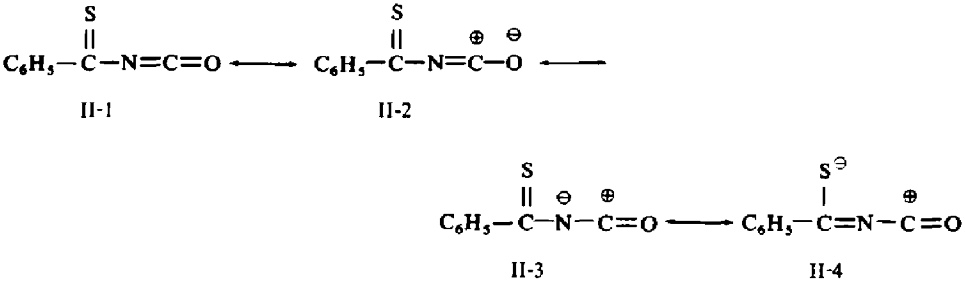
Abstract—The reaction of thiobenzoyl isocyanate with hydrazines is reported. With hydrazine hydrate, 4*H*-5-phenyl-1,2,4-triazole-3(2*H*)-one was obtained in a good yield. In the reaction with mono-substituted phenylhydrazines, 2,3-dihydro-2-aryl-5-phenyl-1,2,4-triazole-3(1*H*)-one or 3-hydroxy-1-aryl-5-phenyl-1,2,4-triazole, or both were formed: the relative amount of the triazoles depended on the nature of the substituents. The reaction with 2,4-dinitrophenylhydrazine, however, gave the semicarbazide which, when treated with aqueous sodium hydroxide or polysphosphoric acid, suffered no ring closure to the triazole. Benzoyl isocyanate reacted with benzylhydrazine, yielding the same triazolone as that obtained from the reaction of thiobenzoyl isocyanate with the hydrazine. The products from these reactions have been identified by independent synthesis as well as IR and UV spectra.

IN THE previous communication[1] in which the reactions of benzoyl (I) and of thiobenzoyl isocyanate (II) with anils or nitrones were investigated, the corresponding 1,2- or 1,4-cycloaddition products were formed in the reaction of I while the reaction of II gave the 1,4-cycloaddition compounds.

On the basis of the above observations and in the other connections,[2] it may be inferred that the contribution of the 1,4-dipolar structure (II-4) in the following resonance structures is strongly manifest in the reaction of II.



$$C_6H_5-\overset{\overset{S}{\|}}{C}-N=C=O \longleftrightarrow C_6H_5-\overset{\overset{S}{\|}}{C}-N=\overset{\oplus}{C}-\overset{\ominus}{O} \longleftrightarrow$$

II-1 II-2

$$C_6H_5-\overset{\overset{S}{\|}}{C}-\overset{\ominus}{N}-\overset{\oplus}{C}=O \longleftrightarrow C_6H_5-\overset{\overset{S^{\ominus}}{|}}{C}=N-\overset{\oplus}{C}=O$$

II-3 II-4

Arcus and Prydal[3] reported that I reacted with hydrazine hydrate to give 1,2-bisbenzoylcarbamoylhydrazine, but with phenyl- or *p*-nitrophenylhydrazine, I afforded 1-phenyl- or 1-*p*-nitrophenyl-4-benzoylsemicarbazide, which underwent ring closure to the corresponding 3-hydroxy-1-aryl-5-phenyl-1,2,4-triazole, when treated with aqueous sodium hydroxide or polyphosphoric acid.

Accordingly, the reaction of II with hydrazine hydrate (III), phenylhydrazines (IV) and benzylhydrazine (V) has been investigated.

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When II was stirred with an equimolar amount of III in xylene at room temperature, yellow crystals (VI) were formed immediately, which turned into colourless crystals with loss of hydrogen sulfide. When the reaction mixture was heated at 100° for a few hr, colourless needles, $C_8H_7ON_3$ (A), m.p. 319·5–320·5° were obtained as the main product, accompanied by a trace amounts of rose-coloured needles, m.p. 186°, which were identical with 1-benzoyl-3-thiobenzoylurea.[1]

After the completion of this work, it was discovered that the reaction of II with III had been independently carried out by Goerdeler and Schenk.[4] They identified the product with m.p. of 321° as 3-hydroxy-5-phenyl-1,2,4-triazole, but its IR spectrum was not given.

The IR spectrum of the compound A showed characteristic bands due to NH and CO group at 3200 and 1740 cm^{-1} respectively, and the NMR spectrum in DMSO-d_6 exhibited singlets at δ 11·85 (1H) and δ 12·20 (1H) ascribed to the NH.

From the above observations, the compound A was assumed to be either 4*H*-5-phenyl-1,2,4-triazole-3(2*H*)-one (VIII) or 2*H*-5-phenyl-1,2,4-triazole-3(1*H*)-one (VIII).

The identity of the compound, m.p. 240°, which was reported by Gehlen[5] was investigated by Mautner and Kumler,[6] and found to be the triazolone VIII. They also identified the product which was obtained by the treatment of 2*H*-5-methyl-1,2,4-triazole-3(1*H*)-one with boiling potassium hydroxide, as 4*H*-5-methyl-1,2,4-triazole-3(2*H*)-one. On the other hand, Bougault and Popovici[7] reported that the reaction of the semicarbazone of phenylglyoxylic acid with iodine and sodium hydroxide gave the triazolone VIII: later,[6] it was suggested that the structure assigned by them to VIII was correct.

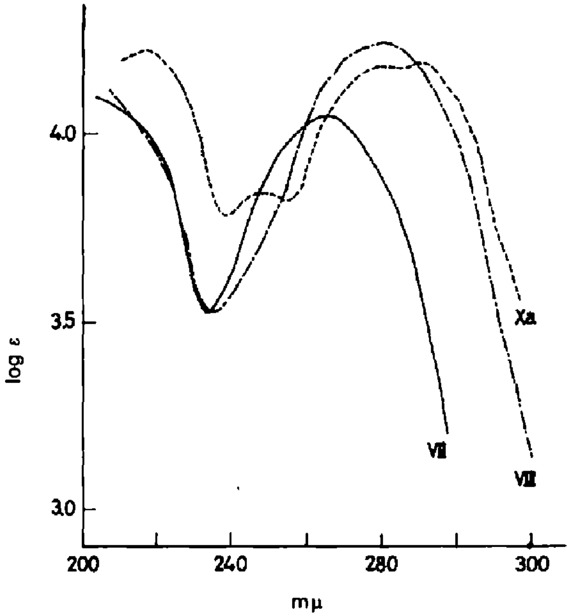


Fig. 1 UV spectra of VII, VIII and Xa in EtOH.

We prepared the triazolone VIII, m.p. 239–240°, by the method of Bougault *et al.*

The IR spectrum of VIII showed well defined bands due to the NH and CO group at 3280, 3120 and 1650 cm^{-1} respectively, and the NMR spectrum in DMSO-d_6 exhibited a singlet at δ 7·40 (2H) ascribed to the NH.

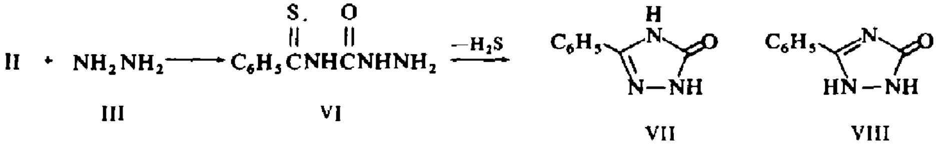
It appears, therefore, that the compound A is VII which is the isomer of VIII. The UV spectra of A and VIII were investigated for evidence of conjugation, which should be absent in the structure of VII, but present in VIII.

As is shown in Fig. 1, the UV spectrum of VIII exhibits absorption compatible with conjugation, but that of A indicates the absence of conjugation. The correlation between the UV spectra of A and VIII is similar to that between the corresponding 5-methyltriazolone isomers reported by Mautner *et al.*[6] Therefore, it is deduced that the compound A is the triazolone VII.

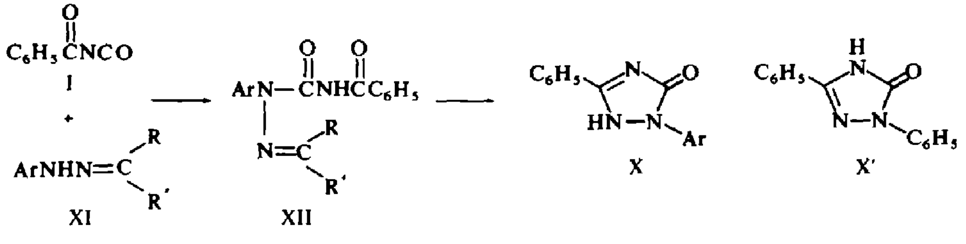
Acetylation of VII with acetic anhydride in pyridine gave the mono-acetyltriazolone, m.p. 239–241°, whose IR spectrum showed characteristic bands at 1770, 1730 and 1705 cm^{-1} respectively. Similar acetylation of VIII gave the mono-acetyltriazolone, m.p. 221°, whose IR spectrum exhibited sharp bands at 1730 and 1650 cm^{-1} in the respective case.*

Even when 2 moles of II were used, no 1,2-bisthiobenzoylcarbamoylhydrazine was formed except VII: II showed a different behavior from I toward III.

These observations suggest that the intermediate yellow crystals are 4-thiobenzoylsemicarbazide (VI), affording VII by evolution of hydrogen sulfide.



In a similar reaction with phenylhydrazine (IVa), II gave colourless needles (Xa), m.p. 230–231°, in a good yield with evolution of hydrogen sulfide. The IR spectrum of Xa showed characteristic bands due to the NH and CO groups at 3100 and 1720 cm^{-1} respectively, and as Fig. 1 shows, its UV spectrum is very similar to that of VIII. Furthermore, the compound Xa was confirmed, by admixed m.p. and IR spectrum, to be identical with the triazolone which was unequivocally prepared from the adduct XIIa, as shown in Scheme 1.



Xa: Ar = Ph; Xb: Ar = p-MeC_6H_4; Xc: Ar = p-ClC_6H_4; Xd: Ar = p-$NO_2C_6H_4$; XIIa: R = R' = Me, Ar = Ph; XIIb: R = H, R' = Ph, Ar = p-MeC_6H_4; XIIc: R = H, R' = Ph, Ar = p-ClC_6H_4; XIId: R = R' = Me, Ar = p-$NO_2C_6H_4$

SCHEME 1

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* It has been reported that the IR spectrum of N-acetyl-3-acetamido-1,2,4-triazole in KBr shows the N-acetyl group band at 1745 cm^{-1}.

Although two triazolone structures for Xa are possible, the above observations are in agreement with the structure of 2,3-dihydro- 2,5-diphenyl-1,2,4-triazole-3(1*H*)-one (Xa) rather than the isomeric 1,2,4-triazole-3(4*H*)-one (X′).

A similar reaction with *p*-tolylhydrazine (IVb) gave colourless needles (Xb), m.p. 232·5°, in good yield. The compound Xb was assumed to be 2,3-dihydro-2-*p*-tolyl-5-phenyl-1,2,4-triazole-3(1*H*)-one by the IR spectrum as well as by the identification with the sample prepared from the adduct XIIb.

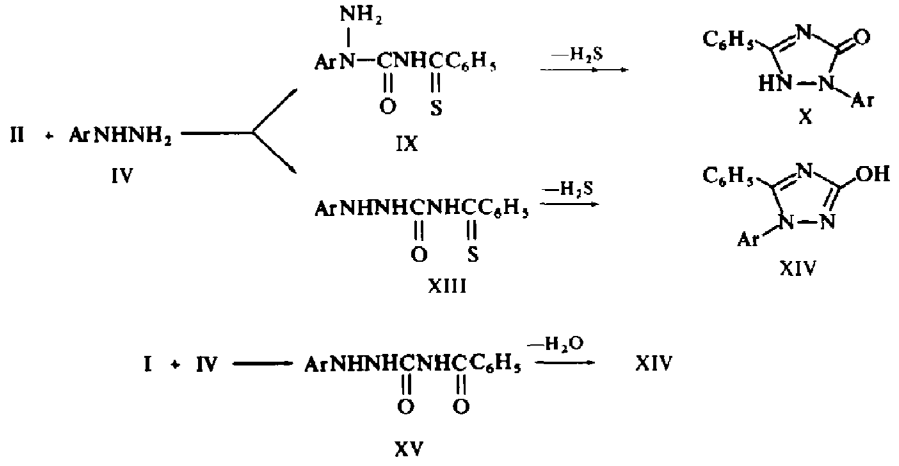
The chemical structures of Xa and Xb are equivalent to the compounds derived from the corresponding 2-aryl-4-thiobenzoylsemicarbazide IXa and IXb by elimination of hydrogen sulfide. No other products were isolated, but it is evident that the probable intermediates IXa and IXb underwent very rapid ring closure.

By a quantitative estimation (described below) it was found that the colourless crystals obtained immediately after the reaction with IVa were contaminated by trace amounts of 3-hydroxy-1,5-diphenyl-1,2,4-triazole (XIVa), but little 3-hydroxy-1,2,4-triazole derivative (XIVb) could be detected in the crystals after the reaction with IVb.

It is expected that II attacks competitively with the α- and β-nitrogen atoms in IV depending on the nature of the substituent in IV.

A similar reaction with *p*-chlorophenylhydrazine (IVc) gave colourless crystals (B) which were difficult to purify. Several fractional recrystallizations from ethanol gave two compounds: one with m.p. of 273° and the other with m.p. of 279–279·5°.

The former was the main product and was identified as 2,3-dihydro-2-*p*-chlorophenyl-5-phenyl-1,2,4-triazole-3(1*H*)-one (Xc) by the IR spectrum as well as by the synthesis from the adduct XIIc, as shown in Scheme 1. The second compound produced in small amounts was identical with 3-hydroxy-1-*p*-chlorophenyl-5-phenyl-1,2,4-triazole (XIVc) which was prepared by the treatment of 1-*p*-chlorophenyl-4-benzoylsemicarbazide (XVc) with aqueous hydrochloric acid.



a: Ar = Ph; b: Ar = $p\text{-MeC}_6H_4$; c: Ar = $p\text{-ClC}_6H_4$; d: Ar = $p\text{-NO}_2C_6H_4$; e: Ar = $2,4\text{-(NO}_2)_2C_6H_3$

SCHEME 2

The IR spectra are illustrated in Fig. 2 for crystals B, Xc and XIVc. As is shown in Fig. 2, the spectra of Xc and XIVc have the characteristic band at 960 or 980 cm^{-1}, besides the CO or OH band respectively.[9]

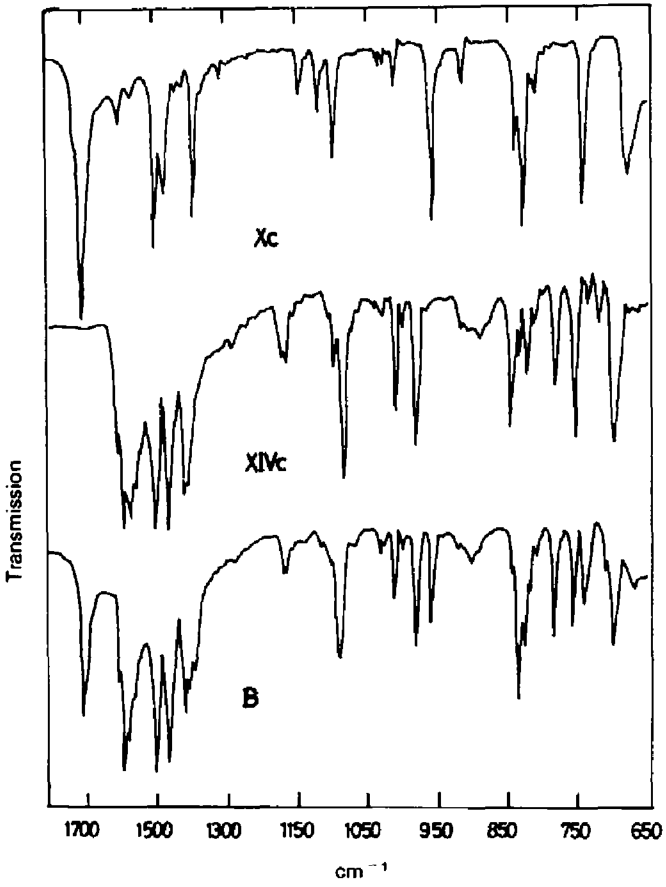


Fig. 2 IR spectra of Xc, XIVc and crystal B in KBr.

Because Xc and XIVc in crystals B were difficult to separate, the quantitative estimation of these compounds was established by the ratio method.[10] It was carried out by the measurement of the absorbances, a_1 and a_2, for the bands at 960 and 980 cm^{-1} respectively. The calibration curves plotting the relationship between a_1/a_2 or a_2/a_1 and the concentration (wt %) of Xc are shown in Fig. 3. According to the calibration curves obtained, it is found that the crude crystals B consisted of Xc (74%) and XIVc (26%).

The reaction with *p*-nitrophenylhydrazine (IVd) gave yellow crystals (C), m.p. 160–200° dec, in a good yield with hydrogen sulfide evolving slowly. Attempts to isolate the probable intermediates, IXd and/or XIIId, from crystals C were unsuccessful because of the cyclization to triazoles during their purification.

When crystals C were treated with aqueous hydrochloric acid, pale yellow crystals which were difficult to purify were obtained. Several fractional recrystallizations from acetic acid afforded two colourless compounds: one with m.p. of 329–330° and the other with m.p. of 275–276°. The former obtained in trace amounts was proved to be 2,3-dihydro-1,2,4-triazole-3(1*H*)-one (Xd). The latter obtained in larger amounts was identical with 3-hydroxy-1,2,4-triazole compound (XIVd).

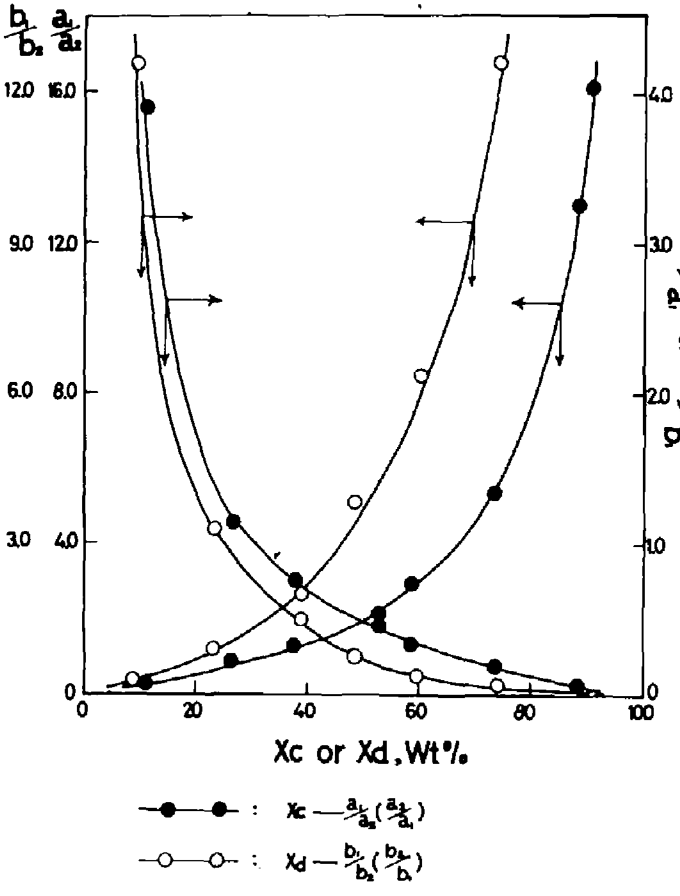


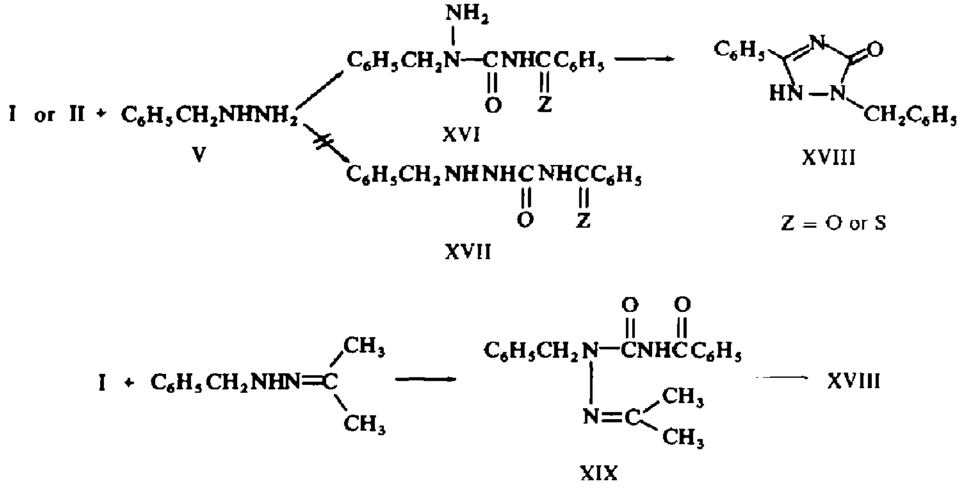
FIG. 3 Calibration curves.

The quantitative estimation of Xd and XIVd in crystals C was established by the ratio method, carried out by the measurement of the absorbancies, b_1 and b_2, for the bands at 960 and 980 cm^{-1} respectively. The calibration curves are shown in Fig. 3. It is found that crystals C consists of Xd (11 %) and XIVd (89 %).

The above observations indicate that the stronger the electron-attractive property of substituent in IV, the more easily the β-N atom in IV is attacked.

The reaction with 2,4-dinitrophenylhydrazine (IVe) at 120° gave yellow needles (XIIIe), m.p. 197°: no hydrogen sulfide was evolved during heating. Furthermore, the treatment of XIIIe with aqueous sodium hydroxide and with polyphosphoric acid brought no further change. On the basis of the nature of the substituent and of elemental analysis, XIIIe was assumed to be 1-(2,4-dinitrophenyl)-4-thiobenzoylsemicarbazide.

On the other hand, the reaction with benzylhydrazine (V) at room temperature gave 2,3-dihydro-1,2,4-triazole-3(1*H*)-one derivative (XVIII), m.p. 221·5°.



SCHEME 3

As I reacts with V to give compound XVIII, the probable intermediate is not 1-benzyl- (XVII, Z = 0) but 2-benzyl-4-benzoylsemicarbazide (XVI, Z = 0). In addition, in the reaction of I with benzylhydrazone of acetone yielded XVIII directly although the adduct XIX was not isolated.

Also, it was found that the thermal cyclization of 1-aryl-4-acylsemicarbazide gave the corresponding triazoles of type X.[11]

EXPERIMENTAL

M.ps and b.ps are uncorrected. IR spectra were recorded on a Nippon Bunko IR-S spectrophotometer and UV spectra were measured in EtOH with a Shimadzu SV-50A spectrophotometer. NMR spectra were determined at 60 Mc with a Japan Electron Optics JNM-3H-60 NMR spectrometer, using TMS as internal reference. Elemental analyses were done by Mr. Eiji Shiozaki.

Benzoyl isocyanate (I). This compound was prepared by the method of Speziale *et al.*,[12] b.p. 100°/24 mm, m.p. 28–29°, ν_{NCO} 2270 cm^{-1}; lit.,[12] b.p. 98°/23 mm, m.p. 25·5–26°, ν_{NCO} (in $CHCl_3$) 2225 cm^{-1}.

Thiobenzoyl isocyanate (II).[1] 2-Phenylthiazoline-4,5-dione[13] (1·0 g) was treated in xylene (5 ml) producing a violent soln of II, which was used *in situ*. This soln is referred as the standard soln of II.

Reaction with hydrazine hydrate (III). To the standard soln of II, III (0·5 g) was added at room temp. The yellow crystals formed evolved H_2S. The reaction mixture was heated at 100° for 4 hr and then cooled. Filtration gave 0·72 g (86%)* of colourless crystals which, on recrystallization from AcOH, afforded 4*H*-5-phenyl-1,2,4-triazole-3(2*H*)-one (VII), m.p. 319·5–320·5°, as colourless needles. (Found: C, 59·38; H, 4·06, N, 26·44. Calc. for $C_8H_7ON_3$: C, 59·62; H, 4·38; N, 26·07%). IR (KBr) cm^{-1}: ν_{NH} 3200, ν_{CO} 1740, 1720 (sh) and 1700 (sh). UV λ_{max}^{EtOH} mμ (ε): 265 (11200).

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* Yields of the products obtained from the reaction of II based on 2-phenylthiazoline-4,5-dione.

The filtrate after the reaction was concentrated *in vacuo* and the residue recrystallized from benzene, gave trace amounts of 1-benzoyl-3-thiobenzoylurea, m.p. 186°, which were identical with an authentic sample.[1]

Acetylation of VII. A soln of VII (60 mg) in pyridine (3 ml) was treated with Ac_2O (1 ml) at 90–100° for 30 min. After cooling, the ppt was collected, washed with water, and dried to give 60 mg of colourless crystals which on recrystallization from EtOH yielded colourless prisms, m.p. 239–241°. (Found: C, 59·02; H, 4·40; N, 21·08. Calc. for $C_{10}H_9O_2N_3$: C, 59·10; H, 4·46; N, 20·68%); IR (KBr) cm^{-1}: ν_{NH} 3150 (sh), 3125 (sh) and 3100, ν_{CO} 1770, 1730 and 1705. This compound was assumed to be either the 2-acetyl or 4-acetyl derivative.

2H-5-*Phenyl*-1,2,4-*triazole*-3(1H)-*one* (VIII).[7] A suspension of the semicarbazone of phenylglyoxylic acid (2·0 g) in 30% Na_2CO_3 aq (70 ml) was treated with I_2 (2·0 g) at room temp. After stirring at the same temp for 30 min, filtration gave colourless crystals (1·5 g), m.p. 239–240°, which, on recrystallization from EtOH, afforded colourless needles (VIII), m.p. 239–240° (lit.[7] 240°). (Found: C, 59·65; H, 4·28; N, 26·39. Calc. for $C_8H_7ON_3$: C, 59·62; H, 4·38; N, 26·07%); IR (KBr) cm^{-1}: ν_{NH} 3240 and 3080, ν_{CO} 1650; UV λ_{max}^{EtOH} mμ (ε): 280 (17100).

Acetylation of VIII. A soln of VIII (0·2 g) in pyridine (5 ml), was treated with AC_2O (3 ml) at 70° for 5 hr, and then allowed to stand overnight. Filtration gave crystals (0·2 g) which, on recrystallization from EtOH, afforded a mono-acetyl derivative, m.p. 221°, as colourless needles. (Found: C, 59·29; H, 4·43; N, 20·89. Calc. for $C_{10}H_9O_2N_3$: C, 59·10; H, 4·46; N, 20·68%); IR (KBr) cm^{-1}: ν_{NH} 3250, 3150 and 3050, ν_{CO} 1730. This compound was assumed to be either the 1-acetyl or 2-acetyl derivative.

Reaction with phenylhydrazine (IVa). A similar reaction with IVa (1·0 g) gave 0·92 g (75%) which on recrystallization from AcOH afforded Xa, m.p. 230–231°, as colourless needles. (Found: C, 70·89; H, 4·44; N, 18·09. Calc. for $C_{14}H_{11}ON_3$: C, 70·87; H, 4·67; N, 17·71%); IR (KBr) cm^{-1}: ν_{NH} 3100, ν_{CO} 1720 and 1700 (sh); UV λ_{max}^{EtOH} mμ (ε): 248 (6860), 280 (15000) and 290 (15300).

This compound was identical with an authentic sample which was quantitatively prepared by the treatment of the adduct XIIa, m.p. 136–137° (lit.[15] 139–140°), with 15% HCl aq at 100° for 1 hr.

The crystals obtained immediately after the reaction were contaminated by trace amounts of XIVa. This compound m.p. 290° (lit.[3] 288–289°), was quantitatively obtained by the treatment of XVa, m.p. 189–190° (lit.[3] 194–195°), with 15% HCl aq at 100° for 30 min; IR (KBr) cm^{-1}: ν_{OH} 2600.

2,3-*Dihydro*-2-p-*tolyl*-5-*phenyl*-1,2,4-*triazole*-3(1H)-*one* (Xb). (a) The reation of II (standard soln) with 0·65 g *p*-tolyl-hydrazine (IVb) at room temp produced a clear soln, before the deposit of crystals with evolution of H_2S. After standing overnight, filtration gave 1·15 g (85%) which on recrystallization from EtOH afforded Xb, m.p. 232·5°, as colourless needles. (Found: C, 71·22; H, 5·14; N, 16·63. Calc. for $C_{15}H_{13}ON_3$: C, 71·77; H, 5·22; N, 16·74%); IR (KBr) cm^{-1}: ν_{NH}: 3080, ν_{CO} 1720 (sh) and 1700.

(b) Compound I (0·84 g) was added dropwise to a soln of the p-tolylhydrazone (1·2 g) of benzldehyde in dry benzene (20 ml) at room temp. After standing for a short while, the benzene was evaporated *in vacuo* leaving 2·0 g which on recrystallization from benzene-petrol b. mixture afforded the adduct XIIb, m.p. 175–176°, as colourless needles. (Found: C, 74·31; H, 5·20; N, 11·75. Calc. for $C_{22}H_{19}O_2N_3$: C, 73·93; H, 5·36; N, 11·76%); IR (KBr) cm^{-1}: ν_{NH} 3390, ν_{CO} 1750 and 1680.

The adduct XIIb (0·5 g) was treated with 10% HCl aq (20 ml) at 90° for 4 hr, yielding 0·31 g (89%) of Xb, m.p. 232·5°. This compound was identical with the product from (a), by the admixed m.p. and IR spectrum.

3-*Hydroxy*-1-p-*tolyl*-5-*phenyl*-1,2,4-*triazole* (XIVb). After I (4·7 g) was added to a soln of IVb (4·0 g) in dry benzene (20 ml), the mixture was allowed to stand for a short while at room temp. Filtration gave 7·2 g, which on recrystallization from EtOH afforded XVb, m.p. 206°, as colourless needles. (Found: C, 67·01; H, 5·55; N, 15·63. Calc. for $C_{15}H_{13}O_2N_3$: C, 66·90; H, 5·61; N, 15·61%); IR (KBr) cm^{-1}: ν_{NH} 3320, ν_{CO} 1720 and 1690.

The compound XVb (2·0 g) was treated with 10% HCl aq (20 ml) at 100° for 3 hr, yielding 1·8 g which on recrystallization from EtOH gave XIVb, m.p. 244°, as colourless needles. (Found: C, 72·06; H, 5·15; N, 16·77. Calc. for $C_{15}H_{13}ON_3$: C, 71·77; H, 5·22; N, 16·74%); IR (KBr) cm^{-1}: ν_{OH} 2600.

2,3-*Dihydro*-2-p-*chlorophenyl*-5-*phenyl*-1,2,4-*triazole*-3(1H)-*one* (Xc). After I (0·77 g) was added to a soln of the *p*-chlorophenylhydrazone (1·2 g) of benzaldehyde in dry benzene (20 ml) at room temp, the mixture was allowed to stand for a few min. The benzene was evaporated *in vacuo*, leaving 1·9 g which in recrystallization from benzene-petrol b. mixture gave the adduct XIIc, m.p. 177–178°, as colourless needles (Found: C, 67·22; H, 4·00; N, 11·14. Calc. for $C_{21}H_{16}O_2N_3Cl$: C, 66·75; H, 4·24; N, 11·13%); IR (KBr) cm^{-1}; ν_{NH} 3380, ν_{CO} 1750 and 1680.

The adduct XIIc (0·5 g) was treated with 10% HClaq (15 ml) at 90° for 4 hr, yielding 0·3 g (84%) of Xc, m.p. 273°. (Found: C, 61·99; H, 3·66; N, 15·36. Calc. for $C_{14}H_{10}ON_3Cl$: C, 61·88; H, 3·71; N, 15·47%); IR (KBr) cm^{-1}: ν_{NH} 3080, ν_{CO} 1720 (sh) and 1700.

3-*Hydroxy*-1-p-*chlorophenyl-5-phenyl*-1,2,4-*triazole* (XIVc). The reaction of I (3·0 g) with IVc (3·0 g) in benzene (20 ml) gave 5·0 g which, on recrystallization from EtOH afforded XVc, m.p. 205°, as colourless needles. (Found: C, 58·12; H, 3·93; N, 14·57. Calc. for $C_{14}H_{12}O_2N_3Cl$: C, 58·03; H, 4·15; N, 14·51%); IR (KBr) cm^{-1}: ν_{NH} 3300 and 3240, ν_{CO} 1720 and 1690.

After the compound XVc (2·0 g) was treated with 15% HClaq (20 ml) at 100° for 2 hr, filtration gave 1·6 g which on recrystallization from EtOH afforded XIVc, m.p. 279–279·5°, as colourless needles. (Found: C, 61·83; H, 3·31; N, 15·97. Calc. for $C_{14}H_{10}ON_3Cl$: C, 61·88; H, 3·71; N, 15·47%); IR (KBr) cm^{-1}: ν_{OH} 2600.

Reaction with p-*chlorophenylhydrazine* (IVc). After IVc (0·75 g) was added to the standard soln of II at room temp, the mixture was allowed to stand overnight with evolution of H_2S. Filtration gave 1·45 g (93%) which, after several fractional recrystallizations from EtOH gave two compounds: one with m.p. 273°, and the other with m.p. 279–280°. The former was the main product and was identical with Xc, by the admixture m.p. and IR spectrum. The latter produced in small amounts was identical with XIVc.

The quantitative estimation by the calibration curves shown in Fig. 3 indicated that the crystals just after the reaction consisted of Xc (74%) and XIVc (26%).

2,3-*Dihydro*-2-p-*nitrophenyl-5-phenyl*-1,2,4-*triazole*-3(1H)-*one* (Xd). After I (2·3 g) was added to a soln of the *p*-nitrophenylhydrazone (3·0 g) of acetone in dry benzene (20 ml) at room temp, the mixture was heated on a water-bath for a few min. Filtration gave 5·2 g which, on recrystallization from pyridine, afforded the adduct XIId, m.p. 203·5° dec, as pale yellow needles. (Found: C, 59·95; H, 4·52; N, 16·52. Calc. for $C_{17}H_{16}O_4N_4$: C, 59·99; H, 4·74; N, 16·46%); IR (KBr) cm^{-1}: ν_{NH} 3220, ν_{CO} 1750 and 1660.

The adduct XIId (4·0 g) was treated with conc HCl (20 ml) at 100° for 1 hr, giving 3·1 g (94%) which on recrystallization from AcOH gave Xd, m.p. 329–330°, as pale yellow needles. (Found: C, 59·67; H, 3·65; N, 19·39. Calc. for $C_{14}H_{10}O_3N_4$: C, 59·62; H, 3·57; N, 19·87%); IR (KBr) cm^{-1}: ν_{NH} 3080, ν_{CO} 1705.

3-*Hydroxy*-1-p-*nitrophenyl-5-phenyl*-1,2,4-*triazole* (XIVd). The reaction of I (6·0 g) with *p*-nitrophenylhydrazine (IVd, 6·0 g) in dioxane (50 ml) at room temp gave yellow crystals (10·8 g) which, on recrystallization from AcOH afforded XVd, m.p. 225° (lit.[3] 226–227°), as pale yellow needles; IR (KBr) cm^{-1}: ν_{NH} 3400 and 3240, ν_{CO} 1720 and 1690.

The compound XVd was treated with conc HCl, but it remained unchanged. According to the method of Arcus,[3] XVd was treated with polyphosphoric acid, giving a quantitative yield of XIVd, m.p. 274–275° (lit.[3] 265–266°), as pale yellow needles. (Found: C, 59·58; H, 3·13; N, 19·94. Calc. for $C_{14}H_{10}O_3N_4$: C, 59·62; H, 3·57; N, 19·87%); IR (KBr) cm^{-1}: ν_{OH} 2600.

Reaction with p-*nitrophenylhydrazine* (IVd). Similarly, the reaction of II (standard soln) with IVd (0·8 g) at room temp gave yellow crystals (1·47 g), m.p. 160–200° dec. These were treated with 15% HClaq (20 ml) at 100° for 1 hr, giving 1·15 g (72%) of pale yellow crystals. Several fractional recrystallizations from AcOH afforded Xd, m.p. 329–330°, and XIVd, m.p. 274°. The quantitative estimation by the calibration curves shown in Fig. 3 indicated that the crystals just after ring closure consisted of Xd (11%) and XIVd (89%). These compounds were proved, by the admixed m.ps and IR spectra, to be identical with the authentic samples.

Reaction with 2,4-*dinitrophenylhydrazine* (IVe). After addition of a soln of IVe (1·0 g) in benzene (10 ml) to the standard soln of II at room temp, the mixture was heated at 120° for 1·5 hr. During this time it turned from dark red to yellow but no H_2S was evolved. After cooling, 1·65 g were filtered off, which on recrystallization from benzene, afforded yellow needles, m.p. 197°. This compound was assumed to be XIIIe. (Found: C, 46·98; H, 2·89; N, 19·07. Calc. for $C_{14}H_{11}O_5N_5S$: C, 46·54; H, 3·07; N, 19·39%); IR (KBr) cm^{-1}: ν_{NH} 3320, ν_{CO} 1720.

When XIIIe was treated with NaOHaq or polyphosphoric acid, it remained unchanged.

2,3-*Dihydro*-2-*benzyl-5-phenyl*-1,2,4-*triazole*-3(1H)-*one* (XVIII). (a) I (1·0 g) reacted violently with the benzylhydrazone (1·2 g) of acetone in benzene (20 ml), giving 1·6 g (84%) which on recrystallization from EtOH gave XVIII, m.p. 222°, as colourless needles. (Found: C, 71·81; H, 4·94; N, 16·75. Calc. for $C_{15}H_{13}ON_3$: C, 71·69; H, 5·21; N, 16·72%); IR (KBr) cm^{-1}: ν_{NH} 3080, ν_{CO} 1720 (sh) and 1690.

(b) The reaction of II (standard soln) with benzylhydrazone (V, 0·8 g) progressed violently, forming colourless crystals with evolution of H_2S. Filtration gave 1·1 g (76%) which, on recrystallization from EtOH, afforded XVIII, m.p. 221·5°, as colourless needles

(c) After a soln of V (1·0 g) in benzene (15 ml) was added to a soln of I (1·2 g) in benzene (10 ml) at room temp, the mixture was allowed to stand overnight. Filtration gave 1·8 g, m.p. 160–190°, which were found to be a mixture of the semicarbazide and triazole by a study of the IR spectrum. The crystals were treated with 15% HCl aq (20 ml) at 100° for 1 hr, giving 1·15 g of XVIII, m.p. 221–222°.

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